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## (54) ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE

(57) An etching solution which contains hydrogen fluoride (HF) and exhibits an etching rate ratio: etching

rate for a boron-glass film (BSG) or boron-phosphorusglass (BPSG)/etching rate for a thermally oxidized film (THOX) of 10 or more at 25°C.

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#### Description

#### **TECHNICAL FIELD**

[0001] The present invention relates to an etching solution, a method for producing an etched article and an etched article produced by the method, more specifically, an etching solution and a method for producing an etched article for selectively etching a doped oxide film, particularly BSG or BPSG relative to an undoped oxide film, particularly THOX, and an etched article produced by the method.

#### 10 BACKGROUND ART

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[0002] Conventionally, as etchants for silicon wafers and the like have been used buffered hydrofluoric acids comprising HF (50% by weight) and NH<sub>4</sub>F (40% by weight) at such a ratio that can achieve a desired etch rate.

[0003] However, the buffered hydrofluoric acids etch not only doped oxide films such as BSG films, BPSG films, phosphosilicate glass (PSG) films, arsenic silicate glass (AsSG) films and the like, but also undoped oxide films such as USG including TEOS (oxide obtained by CVD method using tetraethoxysilane gas) films, THOX and the like. Therefore, the buffered hydrofluoric acids can not selectively etch the doped oxide films.

[0004] An object of the present invention is to provide an etching solution and an etching method for selectively etching oxide films doped with impurities relative to TEOS and THOX.

#### **DISCLOSURE OF INVENTION**

[0005] The present invention relates to the items 1-16 listed below.

25 Item 1: An etching solution comprising hydrofluoric acid, wherein an a ratio of etch rate of a boron silicate glass film (BSG) or boron phosphosilicate glass / an etch rate of a thermal oxide film (THOX) at 25°C is 10 or higher. Item 2: The etching solution according to item 1, wherein a solvent in the etching solution has a relative dielectric constant of 61 or lower.

Item 3: The etching solution according to item 1, the solution containing at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.

Item 4: The etching solution according to item 1, the solution containing (i) water and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 70% by weight or lower.

Item 5: The etching solution according to item 1, wherein the weight ratio of HF: isopropyl alcohol: water is 0.1-50% by weight: 30-99% by weight: 0-70% by weight.

Item 6: The etching solution according to item 1, wherein the weight ratio of HF: acetic acid: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 7: The etching solution according to item 1, wherein the weight ratio of HF: tetrahydrofuran: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 8: The etching solution according to item 1, wherein the weight ratio of HF: acetone: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 9: The etching solution according to item 1, wherein the weight ratio of HF: methanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 10: The etching solution according to item 1, wherein the weight ratio of HF: ethanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 11: The etching solution according to item 1, the solution comprising an inorganic acid.

Item: 12 The etching solution according to item 11, wherein the inorganic acid has a pKa value at 25°C of 2 or lower.

Item 13: The etching solution according to item 11, wherein the weight ratio of HF: HCI: water is 0.01-50% by weight: 1-36% by weight: 0-99% by weight.

Item 14: The etching solution according to item 11, wherein the weight ratio of HF: HNO<sub>3</sub>: water is 0.01-50% by weight: 1-70% by weight: 0-99% by weight.

Item 15: A method for producing an etched article by etching an article to be etched with the etching solution as defined in any of items 1-14.

Item 16: An etched article which is obtainable by the method of item 15.

[0006] According to the etching solution of the invention, the ratio of BSG etch rate / THOX etch rate and/or the ratio of BPSG etch rate / THOX etch rate at 25°C is/are 10 or higher, preferably 20 or higher, more preferably 50 or higher, particularly 100 or higher.

[0007] In case of using TEOS instead of THOX, the ratio of BSG etch rate / TEOS etch rate and/or the ratio of BPSG etch rate / TEOS etch rate at 25°C is/are 5 or higher, preferably 10 or higher, more preferably 50 or higher, particularly 100 or higher.

[0008] The etch rate of the etching solution of the invention can be calculated as the difference in thickness of a film (BSG; BPSG; THOX; TEOS and like USG, etc.) before and after etching divided by etch time.

[0009] The water content is not higher than 70% by weight, preferably not higher than 30% by weight, more preferably about 30-5% by weight. The relative dielectric constant of the etching solution expresses an arithmetic mean of the relative dielectric constants of the components of the etching solutions other than the HF and inorganic acid.

[0010] Preferable examples of the inorganic acid include inorganic acids having a pKa value at 25°C of 2 or lower, for example, hydrochloric acid (pKa=-8), nitric acid (pKa=-1.8), hydrobromic acid (pKa=-9), hydroiodic acid (pKa=-10) and perchloric acid (a pKa-unmeasurably strong acid).

[0011] Examples of the organic acid include acetic acid (relative dielectric constant: 6.15 (20°C)), propionic acid (relative dielectric constant: 3.4 (40°C)), butyric acid (relative dielectric constant: 2.97(20°C)), isobutyric acid (relative dielectric constant: 2.63(71°C)), caprylic acid (relative dielectric constant: 2.63(71°C)), caprylic acid (relative dielectric constant: 2.63(71°C)), dichloroacetic acid (relative dielectric constant: 2.1 (20°C)), dichloroacetic acid (relative dielectric constant: 4.6 (60°C)), monofluoroacetic acid, difluoroacetic acid, trifluoroacetic acid,  $\alpha$ -chlorobutyric acid,  $\beta$ -chlorobutyric acid,  $\alpha$ -chlorobutyric acid, acrylic acid and like monocarboxylic acids, methanesulfonic acid, toluenesulfonic acid and like sulfonic acids, oxalic acid, succinic acid, adipic acid, tartaric acid, citric acid and like polycarboxylic acids.

[0012] Examples of the organic solvent having a hetero atom include methanol (relative dielectric constant: 32.6 (25°C)), ethanol (relative dielectric constant: 24.6 (25°C)), isopropanol (IPA, relative dielectric constant: 19.9 (25°C)), 1-propanol (relative dielectric constant: 22.2 (25°C)), 1-butanol (relative dielectric constant: 17.1 (25°C)), 2-butanol (relative dielectric constant: 15.5 (19°C)), t-butanol (relative dielectric constant: 11.4 (19°C)), 2-methyl-1-propanol (relative dielectric constant: 10.4 (19°C ative dielectric constant: 17.95 (20°C)), 1-pentanol (relative dielectric constant: 13.9 (25°C)), 1-hexanol (relative dielectric constant: 13.3 (25°C)), 1-heptanol, 4-heptanol, 1-octanol (relative dielectric constant: 10.34 (20°C)), 1-nonyla-Icohol, 1-decanol, 1-dodecanol and like alcohols; ethylene glycol (relative dielectric constant: 37.7 (20°C)), 1,2-propanediol (relative dielectric constant: 32.0 (20°C)), 2,3-butanediol, glycerin (relative dielectric constant: 42.5 (25°C)) and like polyois, acetone (relative dielectric constant: 20.7 (25°C)), acetylacetone, methyl ethyl ketone (relative dielectric constant: 18.51 (20°C)) and like ketones; acetonitrile (relative dielectric constant: 37.5 (20°C)), propionitrile (relative dielectric constant: 29.7 (20°C)), butyronitrile (relative dielectric constant: 20.3 (20°C)), isobutyronitrile (relative dielectric constant: 20.4 (20°C)), benzonitrile (relative dielectric constant: 25.2 (25°C)) and like nitriles; formaldehyde, acetaldehyde, propionaldehyde and like aldehydes; ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and like alkylene glycol mono alkyl ethers; tetrahydrofuran (relative dielectric constant: 7.6 (25°C)), dioxane (relative dielectric constant: 2.2 (25°C)) and like ethers, trifluoroethanol, pentafluoropropanol, 2,2,3,3-tetrafluoro propanol and like fluorine alcohols, sulfolane (relative dielectric constant: 43.3 (20°C)), nitromethane (relative dielectric constant: 35.87 (30°C)) and the like.

[0013] The relative dielectric constant of water is 78.3 (25°C).

[0014] The content of HF is about 0.01-50% by weight, preferably about 1-5% by weight.

[0015] The water content is not higher than 70% by weight, preferably not higher than 30% by weight, more preferably about 0-5% by weight.

[0016] The content of the inorganic acid is about 1-99% by weight, preferably about 30-70% by weight.

[0017] The content of the organic acid is about 30-99.9% by weight, preferably about 70-99.9% by weight.

[0018] The content of the organic solvent having a hetero atom is about 30-99.9% by weight, preferably about 70-99.9% by weight.

[0019] The content of at least one member selected from the group consisting of the inorganic acid, organic acid and organic solvent having a hetero atom is about 30-99.9% by weight, preferably about 70-99.9% by weight.

[0020] The inorganic acid has a pKa at 25°C of about 2 or lower, preferably about -5 or lower.

[0021] The relative dielectric constant of the organic acid and organic solvent having an hetero atom is preferably about 40 or lower, more preferably about 10 or lower.

[0022] As the HF is usually used dilute hydrofluoric acid (50 wt. % aqueous solution). However, when the HF does not contain water, 100% HF may be also used.

[0023] In case of HCI, HBr and HI, an anhydrous etching solution can be prepared by blowing these gases through the etching solution.

<sup>55</sup> [0024] Preferable etching solutions of the present invention and their compositions are shown below.

- HF: IPA: water = 1-10% by weight: 70-99% by weight: 0-30% by weight
- HF: acetic acid: water = 0.5-5% by weight: 70-99.5% by weight: 0-30% by weight

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- HF: HCI: water = 0.01-5% by weight: 1-36% by weight: 50-99% by weight
- HF: nitric acid: water = 0.01-5% by weight: 1-70% by weight: 20-99% by weight
- HF: acetone: water 1-10% by weight: 70-99% by weight: 0-30% by weight
- HF: THF: water = 1-10% by weight: 70-99% by weight: 0-30% by weight
- HF: methanol: water = 1-10% by weight: 70-99% by weight: 0-30% by weight
  - HF: ethanol: water = 1-10% by weight: 70-99% by weight: 0-30% by weight

[0025] The etching solution of the invention can be suitably used for selectively etching a doped oxide film of an article to be etched comprising an oxide film (BSG, BPSG, etc.) doped with B, P and the like and an undoped oxide film such as THOX, TEOS and like.

[0026] In the etching method of the present invention, the temperature of the etching solution is about 15-40°C.

[0027] Examples of the article to be etched include single crystalline silicon wafers, gallium-arsenic wafers and like wafers, especially the articles comprising a doped oxide film (BSG, BPSG, etc.) and an undoped oxide film (THOX, TEOS and like USGs).

<sup>5</sup> [0028] The BSG etch rate of the etching solution of the invention is usually about 10-2000 nm/min, preferably about 40-500 nm/min.

[0029] The present invention can provide an etching solution which can selectively etch films doped with impurities, such as BSG, BPSG and the like, relative to THOX, TEOS and like USG, a method for producing an etched article using the etching solution and an etched article.

#### BEST MODE FOR CARRYING OUT THE INVENTION

[0030] The present invention will be explained in more detail with referring to Examples and Comparative Examples below.

Examples 1-2 and Comparative Examples 1-4 (inorganic acid)

[0031] Etching solutions were prepared by mixing HF, water, an organic solvent having a hetero atom (isopropyl alcohol (iPA), THF, acetone, methanol, ethanol), an organic acid (acetic acid) and inorganic acid (HCI, HNO<sub>3</sub>) in the ratios shown in Table 1. Test substrates were produced by forming each of a thermal oxide (THOX) film, USG (TEOS) film, boron silicate glass (BSG) film and boron phosphosilicate glass (BPSG) film on a silicon substrate by CVD method using a tetraethoxysilane gas. The etch rate and etch selectivity of the etching solutions on the test substrates were determined.

[0032] In addition, the etch rate and selectivity of conventional HF-H<sub>2</sub>O and HF-NH<sub>4</sub>F-H<sub>2</sub>O etching solutions were determined in the above-mentioned manner as Comparative Examples.

[0033] The etch rate was determined by measuring the thickness of the films before and after etching with an Auto EL-III ellipsometer manufactured by Rudolf Research.

[0034] The etch rates of the etching solutions were calculated as the difference in thickness of films before and after being etched at 25°C divided by etch time.

[0035] The results of the etching solutions with each composition are shown in Table 1 to Table 8.

[0036] The relative dielectric constant is that of a solvent (an organic solvent having a hetero atom or an organic acid) + water at 25°C, expressed as a calculated value of an average of the relative dielectric constants of the solvent and water having the particular composition.

[0037] Average of relative dielectric constants = [78.3 x (percentage by weight of water) + (relative dielectric constant of solvent at 25°C) x (percentage by weight of solvent)] / [(percentage by weight of water) + (percentage by weight of solvent)]

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BPSG /TEO S sele ctiv ity

	<u></u>	_			_			L.								L				_
	BSG/	TEOS	sele	ctiv	ity	'		34	12	8.5	7.3	40	27	19	10	4.1		9°.6		4.0
	BPSG	/THO	×	sele	ctiv	ity		28	21	17	14	:	ı	,	,	,		1		,
	BSG/	THOX	sele	ctiv	ity			31	17	17	10	09	37	28	15	6.5		6.3		9.9
	BPSG	etch	rate	(A/m	in.)			330	1160	1650	1950	,	,	,	,	1		ı		ı
	BSG	etch	rate	(A/min	•			370	920	1190	1450	120	2200	6500	12000	380		750		1980
	TEOS	etch	rate	(A/m	in.)			11	9/	140	200	m	82	230	1200	63		190		490
	THOX	etch	rate	(A/m	tn.)			12	55	97	140	7	59	350	820	28		120		300
	Relative	dielectric	constant of	solvent	(IPA)+water	(calculated	value)	23.0	35.3	47.6	59.9	21.7	26.4	30.2	34.5	•		1		•
() etchant	Solvent	(IPA)	concen-	tration	€			96	20	20	30	94	80	70	60	0		0		0
ohol (P	Water	-uoo	cen-	tra-	tion	(%)		S	25	45	65	m	10	15	20	66		98		95
oyl alco				tra-	tion	(8)		5	Ŋ	ß	'n	м	10	15	20	1		2		m
HF-H2O-isopropyl alcohol (PA) etchant	Relative	dielectric	constant of	solvent				19.9	19.9	19.9	19.9	19.9	19.9	19.9	19.9	(18.3)		(78.3)		(78.3)
H	Sol-	vent						IPA	(Water	_	(Water	~	(Water							
								Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Comp.	Ex. 1	Comb.	Ex. 2	Comp.

			_	_	_	_			_							_													
BPSG/	TEOS	selec	tivit	>	'				,54	, ;	25	65	) <u>.</u>	ı		ı	ı	1	•	!	•	,		ı	ı	ì	1		
BSG/T	EOS	selec	tivit	>					38	ţ	6	73	?	19		08	84	5	64	7	?	41		23	. 5		10		7.9
BPSG/	THOX	selec	tivit	>		,			75	ŝ	20	16	?	)			ı	•	,			,		,			•		,
BSG/T	НОХ	selec	tivit	>-					. 53		007	94	· ·	100	,	110	120	}	95	ő	}	65		ص 0	,	:	. 17		<u>-</u>
BPSG	etch	rate	(A/mi	٦.					750	9.5	2	1300	:	1	` \	1	,		ì	ı		'		ı	,		,		,
BSG	etch	rate	(A/mi	<u>.</u>					530	0001	7500	1600		2600		3600	4600		8900	1 600		1300	,	2	830		670	000	S .
TEOS	etch	rate	(A/mi	<u></u>					14	٩	9	22		33	•	ۍ, ش	25.5		140	23	}	32	,	ç	85		. 9	72	3
THOX	etch	rate	(A/mi	<u>.</u>	•				01	12	71	17		_ <b>52</b>	Ş	75	0		97	18		50	ç	75	39		40	43	?
Relative	dielectric	constant	of solvent	(acetic	acid)+	water	(calculat-	ed value)	. 88.9	30 1		7.25		7.62	•	0	8.38		9.95	9.80		13.5	9	0.	28.1		35.4	42.7	
Solvent	(acetic	acid) con-	centration	æ)					86	97. 5		97		96	Ų	20	94		06	93.75	-	88.75	76 95		68.75	•	58.75	48.75	
Water	-uacouc	tration	æ							1.25	)	1.5		2		· · ·	m		ท	Ŋ		10	00	;	30		6	20	
HE con-	-	(#) uota	,		•				<del></del>	1.25		1.5	٠	73		?	m	. ,	'n	1.25		1.25	1.25		1.25		1.25	1.25	
Relativ	9 7	Delete	FIC	constan	י סנ	solvent		,	6,15	6.15	)	6.15		6.15	36 3	?	6.15	1	6.15	6.15		6.15	5.15	)	6.15		6.15	6.15	
Solvent				-					Acetic	Acetic	acid	Acetic	acid	Acetic	acto acto	acid	Acetic	acid	Acetic	Acetic	acid	Acetic	Acetic	acid	Acetic	acid	Acetic	Acetic	acid
			_					- 1	EX.	Ex. 10		Ex. 11		Ex. 12	21.		Ex. 14		Ex. 13	Ex. 16		Ex. 17	Ex. 18		Ex. 19		Ex. 20	Ex. 21	

etchant	
(THE)	
HF-H2O-tetrahydrofurane	

<u></u>	_		<u>,</u>	_				Γ			
⊢				ctiv	_			83	20	14	-
BSG/	TEOS	sele	ctiv	ity				130	16	10	a
BPSG	/THO	×	sele	ctiv	ity			110	.27	19	. 4
BSG/	THOX	sele	ctiv	ity	_			170	22	14	-
BPSG	etch	rate	(A/m	in.)				330	830	1200	1,600
BSG	etch	rate	(A/m	in.)				510	069	890	1200
TEOS	etch	rate	(A/m	in.)	•			4	42	82	150
				in.)				3	31	64	110
Relative	dielectric	constant of	solvent	(THF) +water	(calculated	value)		11.3	26.2	41.1	0.82
Sol-	vent	(THE)	con-	cen-	tra-	tion	(8)	06	70	20	20
Water	-uoo	cen-	tra-	tion	(&)			S	22	45	5
ЗH	-uoo	cen-	tra-	tion	(%)	_		J.	ស	ιŊ	ď
Relative	dielectric	constant	of solvent					7.6	7.6	7.6	אר
Sol-	vent			:				THE	THE	THE	AHL
								22	23	24	25
				:				EX.	Ω̈	Š	<u>}</u>

					_				_	_		_
					ity				63	18	11	0
BSG/	TEOS	sele	ctiv	ity					100	15	9.3	ש
BPSG	/THO	×	sele	ctiv	ity				83			14
BSG/	THOX	sele	ctiv	ity					140	18	13	2
BPSG	etch	rate	(A/m	in.					250	520	760	1200
BSG	etch	rate	(A/m	in.)					410	440	620	960
TEOS									. 4	53	67	140
THOX									3	24	49	90
Relative	dielectric	constant of	solvent	(acetone)+	water (cal-	culated	value)		23.7	35.9	48.0	1 09
So1-	vent	(aceto	ne)	-uoo	cen-	tra-	tion	(%)	06	70	20	20
Water	con-	cen-	tra-	tion	(%)				5	25	45	צ
ЗH	-uoo	cen-	tra-	tion	æ ;				2	S	S	u
Solvent Relative	dielectric	constant	of solvent						20.7	20.7	20.7	20.7
Solvent									26 Acetone	Acetone	Acetone	2004000
									26	27	28	20
					:				Ex.	Ex.	Ex.	ć

HF-H20-acetone etchant

HF-H2O-methanol etchant

Relative   HF   Water   Solvent   Relative   THOX   TEOS   BSG   BPSG   BSG   BSG			<u>.</u>			_		_		_	_
Relative   HF   Water   Solvent   Relative   THOX   TEOS   BSG   BPSG   BSG   BPSG				_	_	ity			01	56	0
Relative   HF   Water   Solvent   Relative   THOX   TEOS   BSG   BFSG   BSG   Edition   Con-	BSG/	TEOS	sele	ctiv	ity				6.3	19	1,
Relative	BPSG	/THO	×	sele	ctiv	ity			150	77	0
Relative	BSG/	THOX	sele	ctiv	ity				88	57.	2
Acidetive HF Water Solvent Relative THOX TEOS dielectric con- con- (metha-dielectric etch etch constant cen- cen- nol) constant of rate rate of solvent tra- tra- concen- solvent (A/m (A/m tion tion tration (metha- in.) in.) (%) (%) (%) (%) (%) (%) (%) (%) (%) (%	BPSG	etch	rate	(A/m	1n.)				73	230	017
Action HF Water Solvent Relative THOX dielectric con- con- (metha- dielectric etch constant cen- cen- nol) constant of rate of solvent tra- tra- concen- solvent (A/m tion tion tration (metha- in.) (%) (%) (%) (%) (%) (%) (%) (%) (%) (%	BSG	etch	rate	(A/m	in.)				44	170	730
Relative HF Water Solvent dielectric con- constant cen- cen- nol) of solvent tra- tra- concention tion tration (%) (%) (%) (%) (%) (%) (%) (%) (%) (%)	TEOS	etch	rate	(A/m	in.)				-	5	43
Relative HF Water Solvent dielectric con- constant cen- cen- nol) of solvent tra- tra- concention tion tration (%) (%) (%) (%) (%) (%) (%) (%) (%) (%)	THOX	etch	rate	(A/m	in.)			,	0.5	(J	22
Relative HF Water Solvent dielectric con- constant cen- cen- nol) of solvent tra- tra- concention tion tration (%) (%) (%) (%) (%) (%) (%) (%) (%) (%)	Relative	dielectric	constant of	solvent	(metha-	nol)+water	(calculated	value)	34.0	35.0	30 0
Relative HF dielectric con- constant cen- of solvent tra- tion (%) 32.6 33.6 33.6	Solvent	(metha-	nol)	concen-	tration	æ			94	8	9
Relative dielectric constant of solvent	Water	-uoo	-ueo	tra-	tion	(%)			6	'n	-
<del></del>	HF	-uoo	cen-	tra-	tion	(%)			e	S	9
Solvent	Relative	dielectric	constant	of solvent					32.6	32.6	,
30 31	Solvent								Methanol	Methanol	10000
									30	. 31	ć

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THOX TEOS BSG BPSG BSG/ BPSG BSG/ BPSG etch etch etch THOX /THO TEOS /TEO rate rate rate sele X sele SAM (A/m (A/m (A/m (A/m (A/m (A/m (A/m (A/m	28 23
BSG/ TEOS sele ctiv ity	1
THOX TEOS BSG BPSG BSG/ BPSG BSG/ BPSG etch etch etch THOX /THO TEOS /TEO rate rate rate rate sele X sele S (A/m (A/m (A/m (A/m (A/m ctiv sele ctiv sele in.) in.) in.) ity ctiv ity ity ity	7 9 250 210 36 30
BSG/ THOX sele ctiv ity	36
BPSG etch rate (A/m in.)	210
BSG etch rate (A/m	250
TEOS etch rate (A/m in.).	6
THOX etch rate (A/m in.)	7
Relative THOX TEOS BSG BPSG BSG/ BPSG dielectric etch etch etch etch THOX /THO constant of rate rate rate rate sele X solvent (A/m (A/m (A/m (A/m (A/m ctiv sele thanol)+ in.) in.) in.) in.) in.) ity ctiv calculated value)	27.4
Sol- vent (eth- anol) .con- cen- tra- tion (%)	90
Water con- cen- tra- tion (%)	5
HF Con- cen- tra- tion (%)	. 5
Solvent Relative dielectric constant of solvent	24.6
Solvent	Ethanol
:	Ex.

HF-H2O-ethanol etchant

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Examples)
(Comparative
etchant
HF-NH4F-H20

•	• '				•			
BPSG /TEO S	ctiv ity	,	-	-	-	-	-	l
BSG/ TEOS sele ctiv	ity	0.5	1.3	7.0	0.5	0.4	0.4	0.4
BPSG /THO X Sele	ctiv Tity	,	1	-		-	-	-
BSG/ THOX sele ctiv	ity	9.0	2.2	1.4	6.0	9.0	9.0	6.0
BPSG etch rate (A/m	in.)	-	,	•	-	-	1	1
BSG etch rate (A/m	n.)	110	620	440	350	270	230	200
TEOS etch rate (A/m	in.)	230	480	640	700	720	610	450
THOX etch rate (A/m	· · · · · · · · · · · · · · · · · · ·	170	280	320	400	420	390	300
Sol- vent (water ) con-	cen- tra-	59.9	96	93	88	78	89	59.3
NH4F con-	tion (%)	39.1	2	5	10	20	30	38.7
HF Con- Cen-	•	1	2	2	2	2	2	2
Relative – dielectric constant of solvent	:	(78.3)	(78.3)	(78.3)	(78.3)	(78.3)	(78.3)	(78.3)
Solvent		(Water)	(Water)	(Water)	(Water)	(Water)	(Water)	(Water)
		Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	p. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex.
		Com	Com	Com	Comp.	Comi	Com	Ö

Water         Acid         THOX         TEOS         BSG         BFSG         BFSG         BFSG           con-         concen         etch         etch         etch         rate         rate         rate         rate         rate         rate         rate         rate         rate         sele         X         sele         Sele         X           tra-         n (%)         (A/m         (A/m         (A/m         (A/m         riv         ri	
Acid THOX TEOS BSG BPSG BSG/ BPSG BSG/ Concen etch etch etch etch THOX /THO TEOS tratio rate rate rate rate sele X sele n (%) (A/m (A/m (A/m (A/m ctiv sele ctiv in.) in.) in.) in.) ity ctiv ity ity in.) in.) in.) in.) in.) in.) in.) in.)	
Acid THOX TEOS BSG BPSG BSG/  concen etch etch etch THOX  tratio rate rate rate sele  n (%) (A/m (A/m (A/m (A/m (A/m ctiv  in.) in.) in.) in.) ity  35.9 17 32 440 - 26  35.8 53 89 1200 - 23  35.6 120 200 2500 - 21  35.3 240 380 4500 - 22  83.3 120 170 850 - 19  68.6 240 340 5300 - 22  83.3 120 170 850 - 8.7	
Acid THOX TEOS BSG BPSG concen etch etch etch etch etch etch etch etch	
Acid THOX TEOS BSG concen etch etch etch etch etch etch etch etch	
Acid THOX TEOS concen etch etch tratio rate rate n (%) (A/m (A/m in.) 35.9 17 32 35.8 53 89 35.6 120 200 35.5 180 300 35.5 180 300 35.3 240 380 68.6 240 340	
Acid THOX concen etch tratio rate n (%) (A/m in.) 35.9 17 35.8 53 35.6 120 35.3 240 68.6 240 68.6 240	
Acid concen tratio n (%) 35.9 35.8 35.8 35.8 35.8 35.8 35.8 83.3	
Water con- cen- tra- tron (%) (%) (%) (%) (%) (%) (%) (%) (%) (%)	
#F Con- cen- tra- tion (%) 0.1 0.25 0.75	
pka of H acid co acid co ce ce tr tr ti. ce	12.4 (pKa3)
HF-H <sub>2</sub> O-acid-added Added pka acid aci acid aci HCl -8 7.2	
EX. 34 EX. 35 EX. 36 EX. 36 EX. 37 EX. 38 EX. 39 Comp. Ex.	

#### Claims

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- 1. An etching solution comprising hydrofluoric acid, wherein a ratio of an etch rate of a boron silicate glass film (BSG) or boron phosphosilicate glass / an etch rate of a thermal oxide film (THOX) at 25°C is 10 or higher.
- 2. The etching solution according to claim 1, wherein a solvent in the etching solution has a relative dielectric constant of 61 or lower.
- 3. The etching solution according to claim 1, the solution containing at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.
  - 4. The etching solution according to claim 1, the solution containing (i) water and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 70% by weight or lower.
  - 5. The etching solution according to claim 1, wherein the weight ratio of HF: isopropyl alcohol: water is 0.1-50% by weight: 30-99% by weight: 0-70% by weight.
- 6. The etching solution according to claim 1, wherein the weight ratio of HF: acetic acid: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
  - 7. The etching solution according to claim 1, wherein the weight ratio of HF: tetrahydrofuran: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
- 8. The etching solution according to claim 1, wherein the weight ratio of HF: acetone: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
  - 9. The etching solution according to claim 1, wherein the weight ratio of HF: methanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
  - 10. The etching solution according to claim 1, wherein the weight ratio of HF: ethanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
  - 11. The etching solution according to claim 1, the solution comprising an inorganic acid.
  - 12. The etching solution according to claim 11, wherein the inorganic acid has a pKa value at 25°C of 2 or lower.
  - **13.** The etching solution according to claim 11, wherein the weight ratio of HF: HCI: water is 0.01-50% by weight: 1-36% by weight: 0-99% by weight.
  - 14. The etching solution according to claim 11, wherein the weight ratio of HF: HNO<sub>3</sub>: water is 0.01-50% by weight: 1-70% by weight: 0-99% by weight.
- 15. A method for producing an etched article by etching an article to be etched with the etching solution as defined in any of claims 1-14.
  - 16. An etched article which is obtainable by the method of claim 15.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/06502

			,0133,00302
Int.	CLIFICATION OF SUBJECT MATTER CLIF HOIL 21/306, 21/308, CLIF COPK 13/08		
According to	o International Patent Classification (IPC) or to both na	ional classification and IPC	
B. FIELDS	SEARCHED		
Minimum do Int.	ocumentation searched (classification system followed Cl <sup>7</sup> H01L 21/306, 21/308	oy classification symbols)	
Jits Koka	ion scarched other than minimum documentation to the uyo Shinan Koho 1926-1996 i Jitsuyo Shinan Koho 1971-2000	Jitsuyo Shinan Torok Toroku Jitsuyo Shina	u Koho 1996-2000 n Koho 1994-2000
Electronic d	ata base consulted during the international search (name	e of data base and, where practicable	, search terms used)
C. DOCU	MENTS CONSIDERED TO BE RELEVANT		
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	ered to be of particular relevance describe international filing	understand the principle or theory "X" document of particular relevance	y underlying the invention
date		considered novel or cannot be co	nsidered to involve an inventive
	ent which may throw doubts on priority claim(s) or which is a establish the publication date of another citation or other	step when the document is taken "Y" document of particular relevance	alone : the claimed invention cannot be
	reason (as specified) ent referring to an oral disclosure, use, exhibition or other	considered to involve an inventive combined with one or more other	e step when the document is
means		combination being obvious to a p	person skilled in the an
	ent published prior to the international filing date but later is priority date claimed	"&" document member of the same p	
	actual completion of the international search February, 2000 (09.02.00)	Date of mailing of the international 22 February, 2000	
Name and n	nailing address of the ISA/	Authorized officer	
Japa	anese Patent Office		
Facsimile N	10.	Telephone No.	

Form PCT/ISA/210 (second sheet) (July 1992)

### INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/06502

Category*	Citation of document, with indication, where appropriate, of the releva	nt passages	Relevant to claim No
	Claims (Family: none)	<del></del>	
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